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a<sup>4</sup>  
[0038] The process outlined in Table 1 is a novel decision-support tool for the researcher to use interactively in the development of new catalytic materials. The CDE integrates various modeling tools – computational chemistry, kinetic modeling, and machine learning – with a knowledge management system to house the significant experimental and theoretical knowledge for its efficient future use in the guided development of new catalytic materials.

s  
[0040] With the microkinetic modeling option (step 74), the cycle includes the specification of reactants, products, and intermediates (step 75), the generation of reaction mechanisms (step 76), the screening of mechanisms (step 77), and the identification of critical kinetic parameters (step 78). The screening step (step 77) is further illustrated in FIG. 3b. Referring to FIG. 3b, based on a microkinetic model 90 and experimental data 92, a goodness of fit test is performed (step 92) between the experimental data and the data generated by the model in a process designed to eliminate the reaction mechanisms for which the fit is not good. A second cut is taken by using kinetic parameters calculated using molecular modeling (step 97), and assessing the reasonableness of kinetic parameters associated with the mechanisms (step 96). The relative sensitivity of the catalyst performance to the various kinetic parameters is also assessed (step 98), with a preference expressed for the parameters having the highest levels of sensitivity.

b  
[0041] Returning to FIG. 3a, in addition to the microkinetic modeling, databases of information gathered can be mined using one or more of many types of machine learning and pattern recognition techniques to identify correlations between performance, properties, and preparation variables (step 80). These correlations become the basis for the selection of

6  
Catalyst  
materials. These potential materials can be screened further using Monte Carlo kinetic simulation (step 88). In this step, catalytic performance of a virtual catalyst candidate can be calculated. Using one or a combination of these options, materials are selected for synthesis and testing (step 82), experiments are designed (step 84), and performance and properties are measured in a testing cycle (step 86).

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[0043] Current state-of-the-art molecular modeling of catalysts involves either *ab initio* quantum chemical methods or semi-empirical methods. *Ab initio* quantum chemical methods are first-principle solutions to the Schrödinger equation, involving only a few very basic approximations. Because of the high level of detail and accuracy, they are applicable to essentially any material system but they require high computational intensity. They provide the best accuracy for a wide range of chemical and catalytic properties. These methods are used to examine the chemisorption and reactivity of all reactants, intermediates, and products at different surface coverages in order confirm the reaction mechanism and provide the parameters necessary for detailed microkinetic models (adsorption energies, activation energies, rate constants). In addition, a large set of chemical and catalytic properties are evaluated for different catalytic systems in order to develop a set of property libraries, which are then used to establish correlations (metal-adsorbate bond strengths, site acidity, site basicity, oxidation potential, etc.) and to test hypotheses.

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8  
[0044] Semi-empirical methods include both empirical theoretical models, such as Bond Order Conservation, and semi-empirical quantum chemical methods. Semi-empirical quantum chemical methods attempt to minimize the computational efforts required to solve the Schrödinger equation by approximating multi-center integrals that slow down computation.

These approaches range from very approximate calculations such as extended Hückel calculations, which simply ignore the contributions from multi-center integrals, to very approximate methods using low computational times on the order of a few minutes. More sophisticated methods treat the multi-center interaction integrals using empirical information. They typically use experimental data or *ab initio* results in order to parameterize the integrals.

[0045] In terms of *ab initio* methods, Density Functional Theory (DFT) calculations provide the state-of-the-art for modeling catalytic systems and they can be used to predict chemisorption energies, overall reaction energies, activation barriers, and chemical properties descriptors that target key catalytic properties, such as acidity, basicity, and reducibility. Gradient-corrected DFT methods have proven to be the most robust and accurate methods for the prediction of large transition-metal systems because of their ability to explicitly treat electron-electron correlation. The active surface sites can be approximated by using either a metal cluster model to represent the coordination and bonding of the active metal particles, or a periodic slab model to represent larger exposed surfaces. The accuracy of DFT methods in predicting energetics for transition metal systems is +/- 5 kcal/mol. Although quantitative accuracy is important, the ability to predict the relative trends across the periodic table is more critical for the identification of useful catalyst targets. This enables scanning of a range of unknown systems for optimal metal-adsorbate bond strengths and surface reactivity.

[0046] These detailed calculations can be used to understand and predict the trends in both chemisorption and surface reactivity across the periodic table. Non-local cluster and periodic slab DFT calculations have been used to compute the binding energies of maleic anhydride on the 111 surfaces of Pd, Re, Au, Pd/Re, Pt, Pd/Mo, and Pd/Au. Basic concepts from

frontier molecular orbital theory are subsequently used to construct a general model that is able to predict a priori the outcome of the more detailed *ab initio* calculations. These models provide an understanding of the controlling factors that govern chemisorption as well as a knowledge-driven approach to the screening of multi-metallic and metal oxide systems by simply computing a particular chemical descriptor (in this case the center of the d-band at the surface layer of the metal). This model is further extended to predict activation barriers for different elementary steps in the overall catalytic path. As such, studies show that the reactivity of the surface scaled with the relative location of the d-band center of the metal with respect to the Fermi level. Also, the reaction kinetics over different (111) surfaces is found to correlate quite well with changes in the center of the d-band. There is an optimal trade-off in metal-adsorbate bond strength between different reactions. As the metal-adsorbate bond becomes too weak it becomes difficult to dissociate hydrogen on the surface. This shuts down the overall reaction.

[0047] While DFT quantum mechanical method are appropriate for establishing reaction mechanisms, and for accurately calculating properties for a large number of systems, the calculations can still require 1-2 days per simulation. In order to provide daily guidance and be able to lead high-throughput screening efforts, a much faster method needs to be developed. The present invention uses a variety of semi-empirical methods that run for a few minutes to determine specific catalytic properties within reasonable accuracy. These methods, driven by the scientist, can be coupled with advanced machine learning methods, that are described later, in order to develop a potential set of lead catalytic systems which meet the target properties.

[0048] Another semi-empirical method is the Atomic Superposition Electron Delocalization Molecular Orbital Theory (ASED-MO). ASED may be used to describe many

qualitative features and, in some cases, it can provide quantitative assessments in catalysis. The applicability and accuracy of the approach depends on developing appropriate parameters.

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9.3  
[0049] The present invention generates very detailed *ab initio* libraries as well as empirical databanks, which can be used to parameterize these systems more accurately. By way of simple comparison, we examined how well we can infer trends in binding energies by comparing simple ASED calculation which were optimized to detailed DFT calculations. We found that the results show the correct trends to within 30% for NO, O, and N binding energies over a set of different metals. The application of structural optimization as well as refined regression of the parameters should improve the accuracy to 10-20%.

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9.4  
[0050] In addition to refined ASED models, we have developed a more approximate Bond-Order Conservation (BOC) method. While BOC has some ties back to quantum chemical descriptions of bonding, it is a very simple approach that does not attempt to solve the Schrodinger equation. The approach offers some predictions of reactivity. The present inventors have found that some of the known shortcomings of this method can be overcome by determining interaction parameters from first-principle DFT methods. Also, tight binding or single-SCF DFT methods are used and evaluated for the most appropriate compromise between accuracy and speed.

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9.5  
[0051] Microkinetic modeling incorporates the basic surface chemistry, i.e., elementary steps, in the kinetic description of a catalytic reaction. Such a kinetic model is a very useful tool to compare and extrapolate the performance of different catalytic materials at various process conditions. It is used to eliminate postulated reaction mechanisms that are not consistent

with experimental data. Given a plausible mechanism, microkinetic analysis can also identify the small number of critical kinetic parameters that are required in order to describe the overall rate of the catalytic process. This is accomplished by performing a sensitivity analysis of catalytic performance with respect to all kinetic parameters. Knowledge of the critical kinetic parameters and associated steps can provide the scientist with insights on how to modify materials in order to increase the overall performance.

[0052] In the Catalyst Development Cycle, the microkinetic analysis may include one or more of the following steps:

- 9/12
- (1) *Mechanism enumeration:* Given a catalytic reaction, various possible mechanisms are enumerated based on the list of observed products and possible intermediates, list of plausible elementary steps, experimental kinetic data on a training set of materials, literature data, and chemistry rules. For example, steps that require the simultaneous reaction of more than three reacting species or the breaking and forming of too many chemical bonds are usually not elementary and can be excluded. Reaction pathways can also be computer-generated by assuming again that an elementary step involves only a small number of changes in the bonding of the reactants, i.e., three or four changes in the connectivity of the reactants via bond cleavage and formation.
  - (2) *Mechanism discrimination:* There is usually a deficit of information for the values of kinetic rate constants of elementary steps, especially for the activation barriers. Good estimates of pre-exponential factors can be obtained from collision rate theory and transition-state theory. Molecular modeling

can also be used to constrain the possible values of activation barriers. The remaining unknown kinetic constants become adjustable parameters that are determined by fitting the kinetic model to experimental data. Experimental design methods are used to determine the optimal process variable space for kinetic parameter estimation. Discrimination between two mechanisms is accomplished based on how well each mechanism reproduces the experimental kinetic features as process variables are varied. Additional experimental data may be required for discrimination as the optimal process variable space for mechanism discrimination may differ from the one used for kinetic parameter estimation.

- (3) *Kinetic parameter discrimination:* Mechanisms which can no longer be distinguished based on experimental data (because the process variable space for discrimination is not accessible experimentally) can be examined for the reasonableness of their values of the kinetic parameters
- (4) *Sensitivity analysis:* A sensitivity analysis of the overall catalytic performance with respect to the kinetic parameters of the elementary steps is carried out on the remaining few reaction mechanisms which have passed the steps/filters in (2) and (3). The most sensitive parameters are the critical parameters to be altered
- (5) *Relate critical kinetic parameters to material properties:* This step is probably the most challenging as kinetic parameters may depend on complex combinations of measurable materials properties. Postulated materials



properties may be tested for relevance by synthesizing and testing materials with varying values of that property or by calculating with molecular modeling the critical kinetic parameter and the specific property for a series of model catalytic surfaces. The outcome of that step is one or several structure-property relationships that relate kinetic or thermodynamic parameters to a measurable materials property.

- (6) *Parameter optimization:* Optimum values of the kinetic parameters are calculated from the microkinetic model(s) in the context of the targeted value for the overall catalytic performance. These values are compared to the structure-property relationship in order to assess whether or not a candidate material with the required properties is plausible or not. This information is used to select materials to be investigated in the next iteration of the TC.

[0053] Because the reaction pathway for a catalytic process depends on the properties of the materials, experimental kinetic data on new materials from the TC must be re-processed through steps (2) through (6) in order to investigate possible changes in reaction pathways and to update the kinetic hypothesis and the associated structure-property relationships.

[0054] As in microkinetic analysis, kinetic Monte-Carlo simulations can be used to simulate the rate of elementary surface processes. However, Monte-Carlo simulations take into account the explicit effects of surface coverage, local surface atomic composition, structure, and spatial arrangement. The effects of surface poisons and promoters on catalytic performance can also be simulated. This technique can, for example, simulate the essential features of the kinetics of the catalytic hydrogenation of ethylene on Pd(100). Other simulations are, of course,

possible. The Monte Carlo method successfully describes the relative kinetic trends as process variables are varied and, in some cases where the actual metal surface structure is well defined, it has captured some degree of quantitative accuracy. This approach is unique in relating overall catalytic performance to surface materials properties. While the Monte-Carlo kinetic simulation has been used to elucidate the effects of local structure on the catalytic process, its application to the systematic virtual screening of catalytic surfaces is novel in the CDE. In this invention, it is used to predict the relative performance (activity, selectivity, life - under steady-state and/or transient conditions) of virtual catalytic surfaces as a function of process variables and materials surface properties and to provide relative ranking of these surfaces. Surfaces that show promising catalytic properties can then be explored further experimentally. This tool is aimed at guiding the scientist in the exploration and optimization of catalytic materials.

[0055] As in the micro-kinetic analysis the catalytic process must be broken down into a series of elementary steps or lumped elementary steps. The Monte-Carlo algorithm tracks the spatial and temporal changes of all surface intermediates in order to simulate the kinetics. Values for activation barriers and pre-exponential factors for these steps are necessary input to the model. Pre-exponential factors can be taken from the experimental literature if available or calculated from transition-state and collision rate theories. Activation barriers can be obtained from experiment, *ab initio* calculations or semi-empirical methods such as BOC theory. The latter methods, while less accurate than first-principle quantum chemistry calculations, are considerably faster and thus can be used for fast screening of catalytic surfaces and for their relative ranking. The bond energies of the atomic species used in BOC theory are calculated from *ab initio* computational chemistry. Effects of lateral interactions between

different species as a function of their distance within the catalytic surface grid are separated into through-surface interactions, where the presence of a neighboring adsorbed species affects the local surface electronic properties, and through-space adsorbate-adsorbate interactions. The former can be quantified using BOC theory and the latter using a molecular mechanics models, such as a Force-Field model for example.

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Geo [0056] The Monte-Carlo algorithm examines all reaction scenarios on a combination of different grid sites (atop, bridge, hollow) and different grid ensembles and then assesses their probability of occurrence and rate based on site proximity and occupancy for the reactant and product states of the reaction. When a reaction scenario is possible, binding energies of reactants, products, and intermediates are calculated at the appropriate surface sites. All possible surface scenarios are computed and stored. The overall rate of each elementary step is then calculated based on the number of possible scenarios. Each step is classified as being either in equilibrium or dynamic based on their rate. In the randomly generated time-event, the dynamic reaction that occurs is chosen based on its relative rate as compared to the sum of the rates of all dynamic processes. All equilibrium processes, including surface diffusion, are allowed to occur after every time.

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21 [0058] Machine learning is the process of building from a set of data a data structure, i.e. model, from which new insights, knowledge and learning can be derived. Two possible applications of machine learning in the KC of the CDE are (1) the identification and ranking of critical descriptors or combination of descriptors, including chemical properties such as acidity, basicity, and reducibility, and also process variables important to the preparation and treatment of materials; and (2) the selection of materials candidates or experimental

compositional as well as process parameter regions to be explored experimentally based on the prediction of the learning model. While machine learning techniques have been applied earlier for the development of heterogeneous catalytic materials, their success has been very limited due in part to the small amount of reliable data available and the choice of machine learning methods. The recent development of high-throughput techniques and equipment for the synthesis and assay of catalytic materials is enabling the collection of much larger data sets in a much shorter time and thus is making the application of these data-driven techniques more important and productive in the development of new catalytic materials.

[0060] A schematic diagram of a preferred embodiment of the CDE is shown in FIG 2. The CDE is based on valuable catalyst and reaction knowledge and an understanding that is used to solve catalytic problems. Easy access, retrieval, and archival of this knowledge improves the decision-making ability and productivity of the process. The knowledge system is the information retrieval system that integrates multiple information sources and integrates them in a logical fashion. The information sources include experimental data, modeling, and theoretical data, from literature and from proprietary corporate files. For example, information from kinetic modeling and molecular modeling on reaction elementary steps for a particular catalytic reaction is stored so that it can be re-used easily for a different catalytic reaction which shares one or more elementary steps with the previous reaction. This information may be textual, numerical, structural, or logical, and may reside internally or remotely from the database. The knowledge management system preferably includes an interactive interface for use by the researcher in each step of the process.

23  
[0061] The role of the KC is to greatly augment the scientist's ability and efficiency in retrieving knowledge that is critical to guiding the catalyst development. These tools aim to maximize learning and guide catalyst selection. Critical tasks are described further below.

24  
[0062] Composition/structure, particle size, support, and promoters can affect the surface properties of catalysts. Developing trends relating key surface properties to these parameters will assist the scientist in tuning the catalyst properties. An analysis of existing experimental and theoretical data with machine learning algorithms such as tree analysis can be used to uncover patterns in the theoretical and experimental data even in highly non-linear systems. Data for important descriptors are mined and correlations between performance and these descriptors are developed. Descriptors include synthetic parameters as well as experimental and theoretical bulk and surface properties. This information can be used to construct a working hypothesis for the catalytic reaction, which is tested against new data and improved, at each iteration of the CDE cycle.

25  
[0063] Microkinetic modeling will be used to narrow the list of plausible reaction mechanisms that will be investigated further by molecular modeling. A microkinetic model will be built for various postulated reaction mechanisms. The performance of the materials will be calculated as a function of temperature and reactant and product concentrations for a catalyst training set. Mechanisms that can reproduce general trends in the experimental data will be studied further. Sensitivity analysis will be performed on the rate constants of elementary steps to identify the critical kinetic parameters and how they affect overall performance. These critical

parameters will be related to materials properties using data on a series of materials in order to identify trends more easily, and using scientific prior knowledge and know-how.

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24  
A [0064] Computational chemistry will be used to provide understanding of the reaction mechanism and to confirm/strengthen/propose hypotheses (relating key catalyst properties to kinetic parameters of elementary steps. NDI will use *ab initio* DFT periodic slab molecular modeling techniques in order to examine the elementary surface reaction steps for the reaction. These methods will be used to calculate binding energies, activation barriers, as well as rate constants for elementary steps. Calculated rate constants will be inserted in the microkinetic model. Critical rate constants will be correlated with surface properties in order to identify key material properties. The initial calculations will be done on a catalyst "training" set. The catalyst training set will be synthesized and tested to validate the calculations and identify any limitations of the model. The model will then be refined to account for differences between calculated and observed surface properties and rate constants and to improve the model. As lead catalysts are identified experimentally, the modeling work will focus more specifically on these materials.

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27  
A [0065] Faster semi-empirical methods (calibrated with *ab initio* calculations) are used to calculate kinetic parameters and insert them into a kinetic model. Catalytic performance is calculated as a function of surface composition, structure, and atomic spatial arrangement using Monte-Carlo simulation. This kinetic model can be coupled with an optimization algorithm that assists the search for the optimal catalytic surface using a minimum number of virtual experiments. Theoretical results are validated by comparison with experiments.

28  
[0066] The invention may be better understood by illustration, considering an example. In this example, the CDE is used to identify and optimize commercially viable NO decomposition catalysts for use with lean-burn engines. These new catalysts enable the rapid large-scale commercial use of lean-burn engines and the realization of associated economic and environmental benefits. Currently, catalytic converters for traditional combustion engines are based on three-way catalysts (TWC's), which are incompatible with lean-burn engines.

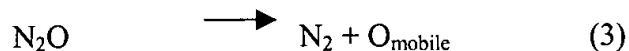
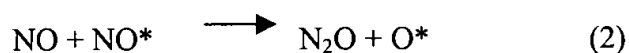
29  
[0067] The key technical barrier for a viable catalyst seems to be the higher affinity of oxygen for the catalytic site relative to the minority NO component – site competition. Since oxygen is present in much higher concentrations, the rate of NO decomposition is too slow. NO decomposition is thermodynamically favored over a wide temperature range of practical interest and the only reaction products are nitrogen and oxygen. The goal of the example of the present invention is aimed at identifying NO decomposition catalytic material that overcome the limitations of current catalysts and would be viable for commercial use.

30  
[0068] Despite extensive research efforts over the past 10-12 years, the currently known catalysts that decompose NO under the oxygen-rich conditions of the lean-burn engine still have severe limitations preventing their commercialization. These limitations include low activity, inhibition by high oxygen levels, poisoning by oxides of sulfur (SO<sub>x</sub>), and inadequate hydrothermal stability. To put the required commercial catalyst performance into perspective, the average rate of NO decomposition (for a 80% removal level) needs to be  $1.3 \times 10^{-4} \text{ mol g}^{-1} \text{ min}^{-1}$ , calculated over the range of temperatures of operation (200-600°C). This rate is about 50 times greater than the estimated rate on the most active catalyst identified to date.

31  
[0071] Noble-metal catalysts are active, as evidenced by their proven performance in the TWCs, but they do not have sufficient NO decomposition activity for lean-burn engine application without serious modification. Supported noble-metal catalysts resist SO<sub>2</sub> poisoning better than Cu-ZSM-5 apparently because of their ability to oxidize the SO<sub>2</sub> to SO<sub>3</sub>.

[0072] The observed rate of NO decomposition on Pt is proportional to (NO)/(O<sub>2</sub>). The reaction is strongly inhibited by O<sub>2</sub>, which competes for adsorption sites with NO. In addition, the presence of O<sub>2</sub> in the feed leads to the oxidation of the Pt surface, and its reconstruction, at high temperatures. The oxidized surface is less active than Pt. The observed rate expression on oxidized Pt resembles that observed on bulk metal oxides, CuO, NiO, Co<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>. On oxides the NO decomposition sites would be oxygen vacancies.

Amirnazmi and Boudart (J. of Catalysis 39, 383-394 (1975)) proposed the following mechanism:



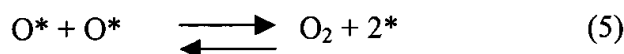
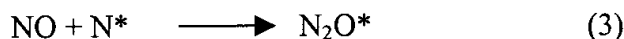
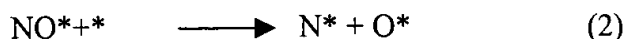
Assuming that step (1) is the rds, step (4) is quasi-equilibrated, and O\* is the most abundant intermediate, this mechanism leads to the rate expression:

$$\text{rate} = k_1(\text{NO})/(1+K_4(\text{O}_2)) \sim k/K (\text{NO})/(\text{O}_2) \text{ with } k = k_1 \text{ and } K = K_4 \quad (\text{Eq. 1})$$

This mechanism invokes the formation of a mobile oxygen atom. N<sub>2</sub>O is observed as product of NO decomposition at low temperatures on Pt



Another possible mechanism for NO decomposition on metals involves the dissociation of adsorbed NO in adsorbed nitrogen and oxygen:



One can derive a similar rate the following rate expression,

$$\text{rate} = k_2 K_1 (\text{NO}) / (1 + \{K_5 (\text{O}_2)\}^{0.5})^2 \sim k/K (\text{NO}) / (\text{O}_2) \text{ with } k = k_2 K_1 \text{ and } K = K_5 \quad (\text{Eq. 2})$$

assuming that step (2) is the rds, steps (1) and (5) are quasi-equilibrated, and O\* is the most abundant surface species. There is no need to invoke mobile oxygen in this case. Based on this preliminary kinetic analysis, a more active catalyst would require an increase in k or a decrease in K. In both mechanisms, decreasing the heat of adsorption of O<sub>2</sub> should result in a decrease in K. This analysis points to the oxygen binding energy as a key descriptor.

[0076] The reaction scheme and corresponding parameters describe reasonably well the experimental data in the absence of oxygen in the reactor inlet (FIGs 3a and 3b). This model explains quite well the observed changes in the rate of NO decomposition with changing inlet NO concentrations. When O<sub>2</sub> is added to the feed, the model over predicts the rate of NO decomposition (an example of which is illustrated in FIG. 4c) suggesting that additional data are needed to adjust the coverage dependence of the heat of O<sub>2</sub> adsorption.